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Selective Synthesis of 1-Alkoxy-3-phenylseleno-1-alkenes and 3-Phenylselenoalkanals by the Reaction of Diisobutylaluminum Phenylselenolate with α,β-Unsaturated Acetals

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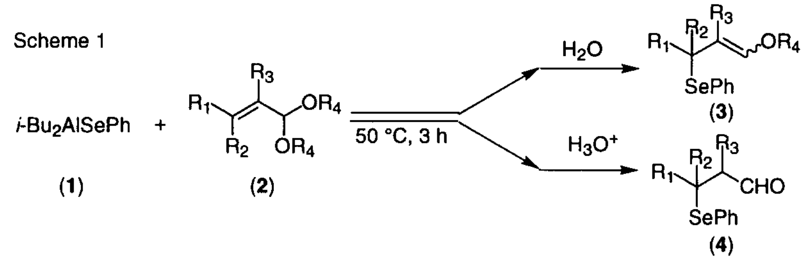
Abstract: The reaction of α,β-unsaturated acetals with diisobutylaluminum phenylselenolate followed by treatment with H_2O affords the corresponding 1-alkoxy-3-phenylseleno-1-alkenes in good yields. When aq. HCl instead of H_2O was employed in the workup, 3-phenylselenoalkanals were formed in good yields.

The chemistry of organoselenium compounds having a selenium-metal bond is of great importance and interest.[1)] Recently, the utilization of organoselenium compounds bearing various selenium-metal bonds was attempted in organic synthesis and these reagents were recognized as useful for the introduction of the alkyl- or phenylseleno function into various compounds and for the reduction of various organic compounds.[2-4)] In our preliminary report, we disclosed a synthetic method of monoselenoacetals by the reaction of acetals with diisobutylaluminum phenylselenolate (i-$Bu_2AlSePh$) (**1**).[2c)] In the course of our study on the development of new synthetic reactions using **1**, we have now found a selective synthetic method of 1-alkoxy-3-phenylseleno-1-alkenes (**3**) and 3-phenylselenoalkanal (**4**) by the reaction of **1** with α,β-unsaturated acetals (**2**) (Scheme 1).

Scheme 1



The treatment of acrolein diethyl acetal with **1**, which was generated *in situ* from diphenyl diselenide and i-Bu_2AlH, in toluene solution at 50 °C for 3 h produced 1-ethoxy-3-phenylseleno-1-propene in 80 % yield with a mixture of stereoisomers (E:Z = 80:20) (entry 1 in Table 1).[5,6)] This reaction exhibits high regioselectivity and 1-ethoxy-1-phenylseleno-3-propene was not isolated at all.[7)] As well as acrolein diethyl acetal, α,β-unsaturated acetals, which have an internal carbon-carbon double bond, gave the corresponding 1-alkoxy-3-phenylseleno-1-alkenes in good yields (entries 2, 4 and 5). Dimethylactals shows the same reactivity as that of the diethyl derivative (entry 6). In the case of cinnamaldehyde diethyl acetal, the yield of product was decreased (entry 7). In this reaction, 3-methylbutenal and geranal diethyl acetal derived from the β,β-dialkylsubstituted α,β-unsaturated aldehydes, were also converted into the corresponding 1-alkoxy-

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Table 1. Selective Synthesis of 1-Alkoxy-3-phenylseleno-1-alkenes and 3-Phenylselenoalkanals

Entry	Substrate	Yield / % $(E/Z)^{a,b}$ 3	4
1	$R_1 = R_2 = R_3 = H$, $R_4 = C_2H_5$	80 (80 / 20)	78
2	$R_1 = CH_3$, $R_2 = R_3 = H$, $R_4 = C_2H_5$	82 (90 / 10)	80
3	$R_1 = R_2 = CH_3$, $R_3 = H$, $R_4 = C_2H_5$	79 (64 / 36)	76
4	$R_1 = C_2H_5$, $R_2 = R_3 = H$, $R_4 = C_2H_5$	75 (68 / 32)	75
5	$R_1 = C_3H_7$, $R_2 = R_3 = H$, $R_4 = C_2H_5$	84 (73 / 27)	82
6	$R_1 = C_3H_7$, $R_2 = R_3 = H$, $R_4 = CH_3$	84 (76 / 24)	81
7	$R_1 = C_6H_5$, $R_2 = R_3 = H$, $R_4 = C_2H_5$	35 (83 / 17)	32
8	$R_1 = (CH_3)_2C{=}CHCH_2CH_2$, $R_2 = CH_3$, $R_3 = H$, $R_4 = C_2H_5$	76 (72 / 28)	72

a) Isolated yields. b) The ratio of E and Z was determined by ^1H NMR.

3-phenylseleno-1-alkenes unaffected by the steric hindrance by the β alkyl group (entries 3 and 8).

When 1-ethoxy-3-phenylseleno-1-propene was treated with aq. HCl, the hydrolysis of the vinyl ether function proceeded to afford 3-phenylseleno-pentanal in quantitative yield. We next examined the one pot synthesis of 3-phenylselenoalkanal (**4**) based on the reaction of α,β-unsaturated acetals with **1** and subsequent hydrolysis with aq. HCl. The results of the synthesis of various 3-phenylselenoalkanals by using this one pot method are also shown in Table 1.[7]

In summary, the selective syntheses of 1-alkoxy-3-phenylseleno-1-alkenes and 3-phenylselenoalkanals based on the reaction of α,β-unsaturtaed acetals with i-$Bu_2AlSePh$ have been developed. Further investigations along these lines are now in progress.

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References and Notes

1) a) A. Krief and L. Hevesi, in "*Organoselenium Chemistry*," Springer Verlag, Berlin (1988), Vol. 1; b) C. Paulmier, in "*Selenium Reagents and Intermediates in Organic Synthesis*," Pergamon Press, Oxford, (1986); c) S. Patai and Z. Rappoport, in "*The Chemistry of Organic Selenium and Tellurium Compounds*," Vol. 1 and 2, (1986) and references cited therein.

2) The synthetic applications of organoselenium compounds having Se-Al bond: a) M. J. Dabdoub, T. M. Cassol, A. C. F. Batista, *Tetrahedron Lett.* **1996**, *37*, 9005. b) T. Inoue, T. Takeda, N. Kambe, A. Ogawa, I. Ryu, N. Sonoda, *J. Org. Chem.* **1994**, *59*, 5824. c) Y. Nishiyama, S. Nakata, S. Hamanaka, *Chem. Lett.* **1991**, 1775. d) K. Maruoka, H. Yamamoto, *Angew. Chem. Int. Ed. Engl.* **1985**, *25*, 668. e) B. A. McKittrick, B. Gamem, *J. Org. Chem.* **1985**, *50*, 5897. f) K. Maruoka, T. Miyazaki, M. Ando, Y. Matsumura, S. Sakane, K. Hattori, H. Yamamoto, *J. Am. Chem. Soc.* **1983**, *105*, 2831. g) A. P. Kozikowski, A. Ames, *J. Org. Chem.* **1978**, *43*, 2735.

3) For recent reviews of the utilization of compounds having Se-B and Se-Si; see L. A. Paquette Ed. in "*Encyclopedia of Reagents for Organic Synthesis*" John Wiley & Sons Vol. 1-6 (1996).

4) For examples of organic syntheses using selenium compounds having Se-Sn bond; Y. Nishiyama, H. Ohashi, K. Itoh, N. Sonoda, *Chem. Lett.* **1998**, 115 and references cited therein.

5) To a toluene (5 ml) solution of PhSeSePh (0.5 mmol) was added a small excess amount of a 1.5 M toluene solution of i-Bu_2AlH (1.2 mmol) at 0°C and the solution was stirred at that temperature for 30 min. α,β-Unsaturated acetal (1.2 mmol) was added to the resulting solution and stirred at 50 °C for 4 h. After the reaction, H_2O or 1M HCl (15 mL) was added to the reaction mixture, extracted with diethyl ether (20 mL x 3) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting oil was isolated by column chromatography on silica gel to give the corresponding 1-alkoxy-3-phenylseleno-1-alkenes or 3-phenylselenoalkanals.

6) When the reaction of α,β-unsaturated aldehyde with **1** was carried out, side reactions took place to afford complex mixtures.

7) Although Yamamoto et al. reported that the alkylation of chiral α,β-unsaturated acetals with Me_3Al (or i-Pr_3Al) proceeded smoothly to yield 1,4-adduct preferentially, the reason of high regioselectivity was not disclosed on this manuscript, see: J. Fujiwara, Y. Fukutani, M. Hasegawa, K. Maruoka, H. Yamamoto, *J. Am. Chem. Soc.* **1984**, *106*, 5004.